Generation of Mathematical Rules Governing Cellular Automata (CA) Predictions of Microstructural Evolution

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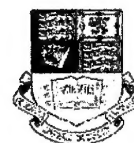**for**
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13. ABSTRACT (Maximum 200 words)

This report results from a contract tasking Imperial College, Department of Materials as follows: The contractor will be required to accomplish the following tasks: prepare preliminary report outlining the primary direction of research and structure for interim report. Prepare a detailed interim report on rules governing cellul tmata simulations of microstructural evolution and participate in an international forum on intelligent processing and manufacturing of materials.

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Executive summary

Objectives

To assess the feasibility of bridging the gap between atomistic scale and microstructural scale modelling.

Why

If we can understand how variations on the atomistic level modify the microstructure, we will be in a position to engineer microstructures by making modifications at the atomic level.

Approach

The possible approaches to the generation of parsimonious rules for the Cellular Automata (CA) engine from atomistic scale simulations were first reviewed (see preliminary report) and here we demonstrate the feasibility by addressing a specific problem.

Conclusions

1. CA can be used to simulate microstructural evolution using rules generated by atomistic simulations.

2. This was demonstrated using the specific example of the adsorption/desorption of inert gas atoms on a Ca (111) surface.

3. The computational benefits if using atomistic based rules cellular automata (AR-CA) are considerable. We have shown a computational gain over MD simulations of the same size of 10^5.

4. The computational gain can be increased significantly by using multiple atom CA cells of a hierarchical approach.

5. Specific conclusions from the first implementation of an AR-CA model are:

    i. island growth is observed;

    ii. island growth is a strong function of temperature and gas atom species; and

    iii. island growth rates depend on the radius of the boundaries - consequently, a ripening process of island growth is observed over a specific temperature range.

Table of Contents

Simulating the Evolution of an Atomic Layer of Neon or Argon on a Calcium (111) Surface Using Atomistic Based Cellular Automata Rules

1 Motivation

Cellular automata (CA) methods are computationally simple and as such are attractive alternatives to Molecular Dynamics (MD) and Monte Carlo (MC) methods for simulating the dynamic evolution of solid state systems. This is particularly true in the present context where we wish to simulate microstructural evolution at the atomic level. As will become clear, the size of the growth structures associated with the gas atom layers requires us to consider 40,000 gas atom sites. Furthermore, we find that microstructure can evolve slowly with respect to the association and evaporation of gas atoms which implies that many tens of thousands of atomic vibrations would have to be simulated explicitly if an MD method were to be employed. This would be a major undertaking for an MD code whereas using CA it can be carried out in a matter of minutes on a machine of modest power.

Of course, the system we will consider here is rather specific and not itself of great technological importance. However, to the authors knowledge, this is the first time that atomistic simulation data has been used as the basis for CA rules. As such, this study presents a powerful new methodology for bridging between atomistic and microstructural scale simulations.

2 The Problem

We will describe the evolution of a single layer of neon or argon on a calcium (111) surface. This is treated as a two dimensional problem, thus it is assumed that if gas atoms do form a second covering layer, this is not of any significance to the evolution of the first layer.

Since this is an atomic scale problem, it is necessary to account explicitly for the interaction between a gas atom and the calcium surface and between a gas atom and its neighbouring gas atoms (inter gas atom interactions). Interatomic potentials were therefore derived which describe the interaction energy between atomic species as a function of interatomic separation (these will be described in detail below). Thus, once we know the position of a gas atom on the surface and its number of neighbouring gas atoms, it is straightforward to determine its stability. In the approach used here, these energies are translated into local rules for the CA engine.

The starting point for all the simulations described here is a bare metal surface. The gas atom layer is deposited onto the surface, from the gas phase, as a flux whose magnitude can be varied. Gas atoms may also desorbe from the surface. The surface therefore evolves via a combination of adsorption and desorption processes both of which are temperature dependent via the CA rules.

Clearly it is essential to understand the physical basis of the CA rules. Thus in the next section we will consider the (111) surface structure and the positions of the gas atoms in detail.

2.1 Crystallography

Calcium metal has an FCC structure so that the (111) surface exhibits a close packing of Calcium atoms. These may be regarded as "A" sites. When a gas atom attaches itself to the surface it will sit in a site which is formed by three metal atoms since this maximizes its interaction with the metal surface. It is clear from the figure below that two sets of interstitial sites exist, these can be regarded as "B" sites and "C" sites.
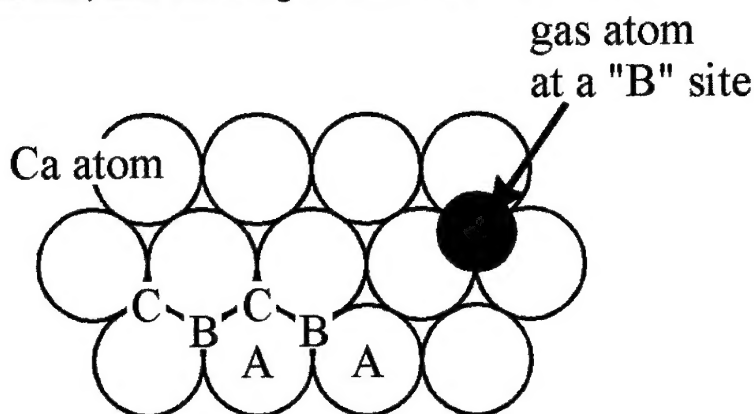
If we examine the (111) surface more closely it is clear that the distance between an interstitial "B" site and a nearest neighbouring "C" site is rather short. Indeed the gas atom in the figure above (which represents neon in scale to calcium) overlaps considerably onto the "C" site. As such, if a gas atom resides in a "B" site, it is not possible for a second gas atom to occupy an nearest neighbour "C" site due to steric hinderence. It is important to realise that this is true only because of the specific matching of the size of the Ca (111) surface to the sizes of the Ar and Ne ions.

Let us now consider the evolution of the gas atom layer as follows. When the first few gas atoms impinge on the surface, they may reside in either A or B sites. As more atoms collect, patches or islands of B-type and C-type atoms form. In the diagram below, it is clear that the distance between two nearest neighbour B-type gas atoms is the same as between two C-type gas atoms. However, the distance between allowed, none hindered B-type and C-type atoms is greater. This results in an area of surface with a lower density of gas atoms which will be termed a growth fault. In three dimensions, it would give rise to a stacking fault. This is important to the stability of a gas atom on the surface since when gas atoms interact over a longer distance, their interaction energy is lower. Indeed, this is the driving force which results in the formation and growth of islands of gas atoms which are occupying only one type of site.

Growth
Fault

gas atoms at "B" sites

Growth
Fault

gas atoms at "C" sites
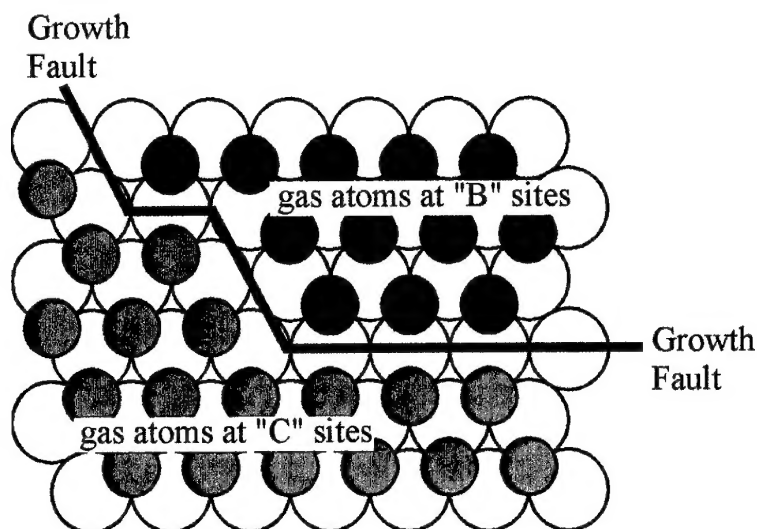
2.2   Interatomic potential functions

Inert gas atoms interact through two terms, electron cloud overlap repulsion and van der Waals attraction. In this study, these are manifest in Lennard-Jones potentials where, if r_{ij} is the distance between atoms i and j, the interaction energy, E_{ij}, is given by:

$$E_{ij} = Ar_{ij}^{-12} - Br_{ij}^{-6}$$

where A and B are constants specific to atoms i and j. For each potential type, the constant "B" corresponds to the van der Waals interaction and can be determined from the polarisabilities of the interacting ions via the Slater Kirkwood formulae (see Fowler et al. *Mol. Phys.*, **56**, 83, (1985)). For the inert gases, the "A" constants were determined by ensuring that the appropriate potential reproduced the lattice parameter of the inert gas lattice (note that both neon and argon exhibit FCC latticies). For the inert gas - metal interaction, the "A" parameter was chosen so that the potential has a minimum corresponding to r_{ij} = gas radius + metal radius.

Table I: Interatomic Potential Parameters

Potential type	A (eVAng^{12})	B (eVAng^{6})
Ca - Ne	12276.6	12.54
Ca - Ar	64447.4	40.90
Ne - Ne	1953.89	4.14
Ar - Ar	53845.3	40.90

Once the parameters have been determined, it is possible to calculate the interaction energies, which define the stability of an atom at a specific site on the surface. Usually with atomistic simulation, a calculation would be carried out during which all atoms

would be allowed to relax to zero force. In ionic systems, where long range Coulomb forces operate, this is critical. However, in this highly symmetric system, where energies are described by short range van der Waals interactions, a more simple approach is justifiable. First, the interaction of a gas atom with the substrate is given by three times the energy of interaction of a gas atom with a single calcium atom at; r_{ij} = gas radius + metal radius. Second, the interaction energies between nearest neighbour "B" gas atoms is given by the value of the potential at; r_{ij} = Ca - Ca nearest neighbour distance = twice the Ca metal ion radius. Remember, the separation of the gas atoms is defined by the substrate. The same is true for interactions between nearest neighbour "C" gas atoms. The total interaction between a gas atom and its nearest neighbours depends on the number of nearest neighbours. This is, of course, a key feature of the model.

A further simplification is made to describe the interactions between "B" site gas atoms and nearest allowed "C" site gas atoms: they are assumed to be zero. Although this may seem a somewhat draconian assumption, the increase in the gas - gas distance in the (2,-1,0) direction (hexagonal coordinate system) over the nearest "B" - "B" is 1.5366 which implies a reduction in the gas - gas interaction by a factor of 13. The reduction in interaction in the (0,1,-1,0) direction is somewhat less, a factor of 2.2. Given this, it would be interesting, in future work, to account for the "B" - "C" interaction in the (0,1,-1,0) direction which may lead to some anisotropic growth effects.

Given the above rules, it is simple to calculate the energy that a gas atom would experience if it were to occupy a specific surface site. This will be known as the attachment energy, E_a. Note that because of the way that the interaction potentials are defined, negative attachment energies are favourable.

This leaves us with the problem of relating the attachment energy to;

i). The probability that a free gas atom, incident on the surface, will become attached to the surface and

ii). That over a given time period, an attached gas atom will desorbe from the surface.

This will be the subject of the next two sections.

2.3 Adsorption

The probability for adsorption is the fraction of incoming atoms that become attached to the surface, P_{att}. The incoming atoms are assumed to have a Maxwell distribution of kinetic energies, *e*;

$$n(e) = (1/kT)\exp(-e/kT)$$

The fraction of incoming atoms that stick to the surface depends on the substrate's ability to dissipate a sufficient proportion of the kinetic energy of a colliding atom for the atom to become trapped in the potential well. Thus, we make the assumption that any atom with kinetic energy less than E_a will stick. Thus;

$$P_{att} = \int_0^{E_d} \frac{1}{kT} \exp(-e/kT)de = 1 - \exp(-E_a/kT)$$

2.4 Desorption

Assuming a single step activated process, the probability, P_{des}, that desorption occurs between t and t + dt is given by;

$$P_{des}(R_d,t) = R_d \exp(-R_d t)$$

where the desorption rate, R_d, is given by;

$$R_d = g_d f_o \exp(E_a/kT)$$

where T is temperature in Kelvin, k is Boltzmann's constant, g_d is a geometric factor (which we take to be unity in this case) and f_o is the attmept frequency. Thus, the total number of atoms which desorbe over a single time step, s_t is;

$$P_{des} = \int_0^{s_t} R_d \exp(-R_d t)dt = 1 - \exp(-R_d s_t)$$

The attempt frequency is, to a good approximation, equivalent to the vibrational frequency of the gas atom on the surface. This can be determined from the interatomic potentials. Here the energy of each gas atom was determined as a function of its distance perpendicular to the surface, assuming a full compliment of neighbouring gas atoms (i.e. a symmetric site). Harmonic functions were then fitted to each energy profile to yield the force constants. The characteristic frequencies were then determined from the force constants: these were 4.45×10^{10} s^{-1} for Ar and 4.59×10^{-1} s^{-1} for Ne.

If the attempt frequency is not known, it can be assumed to be equal to the reciprocal of the time step, in which case, the desorption probability simplifies to;

$$P_{des} = 1 - \exp\{(\exp-E_a/kT)\}$$

which is approximately equal to $\exp(-E_a/kT)$ when the value of E_a/kT is small. However, if this approximation is made, we cannot relate the flux to any real time scale and the only simulations that are definitive are those that run to equilibrium.

2.5 The flux

In this work, the flux is defined to be;

$$f_N = \frac{(\text{number of atoms striking the surface})}{(\text{number of surface sites})(\text{time step})}$$

This is an atomistic model which naturally lends itself to the implementation of the type of relationship discussed above. The flux used here was 15%, that is, the number of gas atoms which were allowed to interact with the surface corresponded to 15% of the total number of surface sites (B and C). It is important to realise that some of these atoms could attempt to interact with the same surface site. In this case, only one atom is allowed to be successful. This way of implementing the flux is realistic since gas atoms interact with the surface continuously rather than in the step wise discrete manner of CA. However, if two atoms attempt to simultaneously occupy nearest neighbour sites, none are allowed to be successful. This is not physically realistic for the long CA time steps used, but it is computationally much simpler than any alternative choice algorithm yet discovered.

Once the flux value is chosen, for a given box size, this defines the number of gas atoms, each of which are assigned a random number from 1 to the total number of surface sites. Integer division by 2 is then carried out to yield an integer and a remainder. If the remainder is zero, the atoms will strike a "B" site, if it is one, it will strike a "C" site. The integer value assigns the atom to a surface cell which contains a "B" site and a "C" site. The number of surface cells is, of course, half the number of surface sites.

It would be a great advantage to be able to relate the flux to the pressure of the gas above the surface. In this case, we can define the flux in terms of the number of atoms striking a surface area in unit time and relate this to the velocity of an ideal gas.

$$\frac{(\text{number of atoms striking the surface})}{(\text{surface area})(\text{time step})} = \frac{pc^*}{kT}$$

where p is the partial pressure of the gas and c^* is the mean velocity of the incoming atoms. Then,

$$c^* = \left(\frac{8kT}{\pi M}\right)^{1/2}$$

so that the flux can be related to the pressure by

$$f_N = \frac{p}{2d_s}\left(\frac{8}{\pi MkT}\right)^{1/2}$$

where d_s is the surface density of absorption sites and M is the mass of the absorbing species.

3 The CA rule set

To a great extent, the CA rule set is defined by the ideas introduced in the preceding sections. These can now be presented formally.

3.1 Site selection or flux rules

These concern the assignment to the incident atoms, of a single random number which determines which surface cell the atom will strike and weather that will be to the "B" or "C" site within that cell.

The first rule *assigns to each atom incident on to the surface a random number from one to the total number of surface sites.*

This number then undergoes integer division by two.

The second rule uses the value of the remainder from the integer division. *If the remainder is zero, the atom is incident on to a "B" site, if the remainder is one, the atom is incident on to a "C" site.*

The third rule uses the integer value from the integer division. *The integer value assigns the atom to a particular cell on the surface.*

The combination of a surface cell and the assignment of "B" or "C" site yields a unique interstitial site.

3.2 Unavailable site rules

The first rule concerns occupied sites. *When the flux directs a gas atom to an interstitial site that is already occupied, the gas atom will not become attached to the surface.*

The second rule concerns the hinderence that an occupied "C" site has to "B" site occupation and vice versa. *When the flux directs a gas atom to a "B" interstitial site that has a gas atom at a nearest neighbour "C" site, the gas atom will not become attached to the surface.* There is an equivalent hinderence rule for gas atoms directed to a "C" site.

3.3 Available site attachment rule

This rule concerns the probability of a gas atom becoming attached once it has been determined that a site is available for occupation. It assumes that the attachment energy, E_a has been calculated. *The probability, $P_{att}(E_a)$, that a gas atom will become attached to the site, to which it has been directed to by the flux, is given by a Bolzmann factor;*

$$P_{att}(E_a) = 1 - \exp(E_a/kT)$$

3.4 Detachment rule

Within the approximations discussed above, at each time step, all attached gas atoms are given the opportunity to desorbe. *The probability that a gas atom will desorbe from the surface, $P_{des}(R_d)$ is given by a Bolzmann factor;*

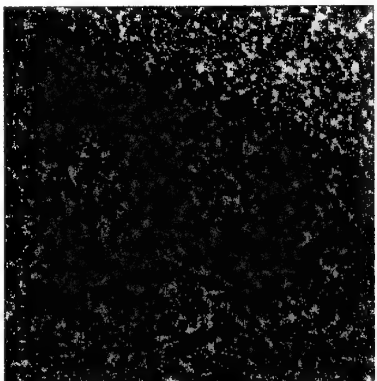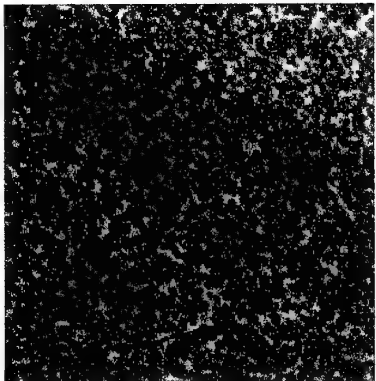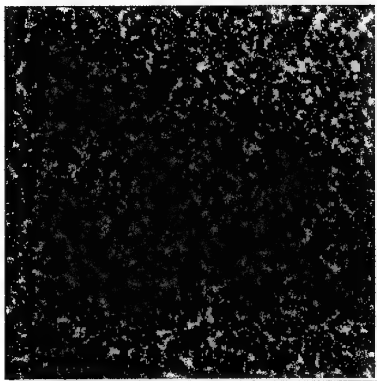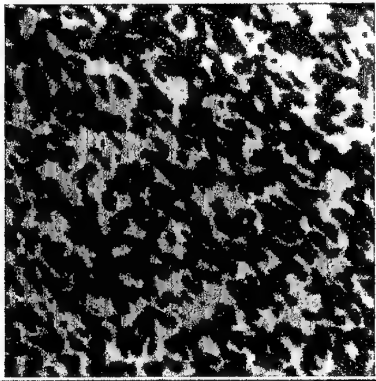$$P_{des}(R_d, s_t) = 1 - \exp(-R_d s_t)$$
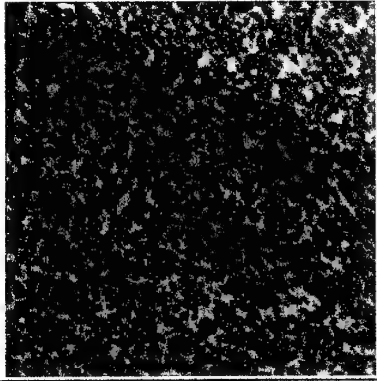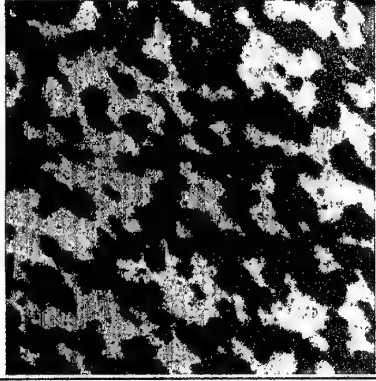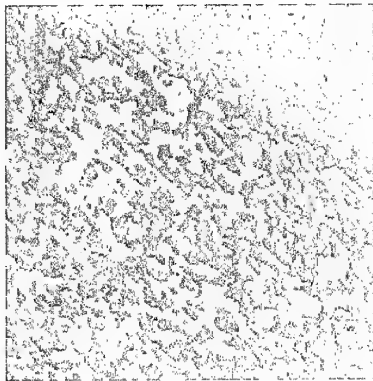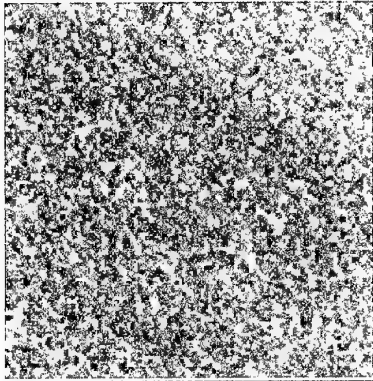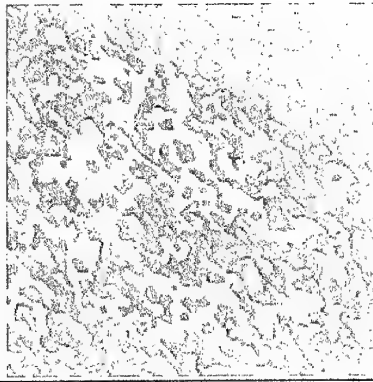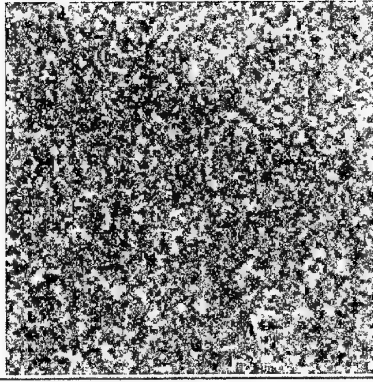
4 Visualization
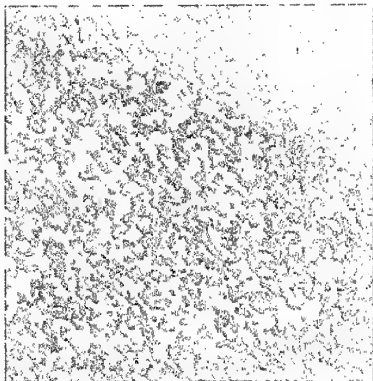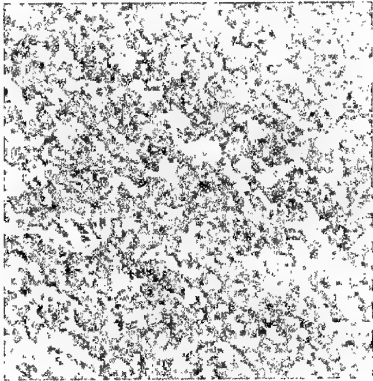
To perform the calculations, the program uses a diamond portion of the hexagonal lattice. In the results discussed here, this was chosen to be 200 by 200 sites, i.e. 40,000 sites in total. Each pair of sites on the surface is indexed by coordinates i and j as shown in the figure below. Each site in a pair is indexed by a 1 or 2. In order to minimize memory usage, the results of the calculations are shown on a square grid rather than a diamond grid, allowing one pixel to represent one cell. The colour red indicates that site 1 of cell (i,j) is filled, the collar blue indicates that site 2 is filled, and the collar black indicates that neither site is filled.
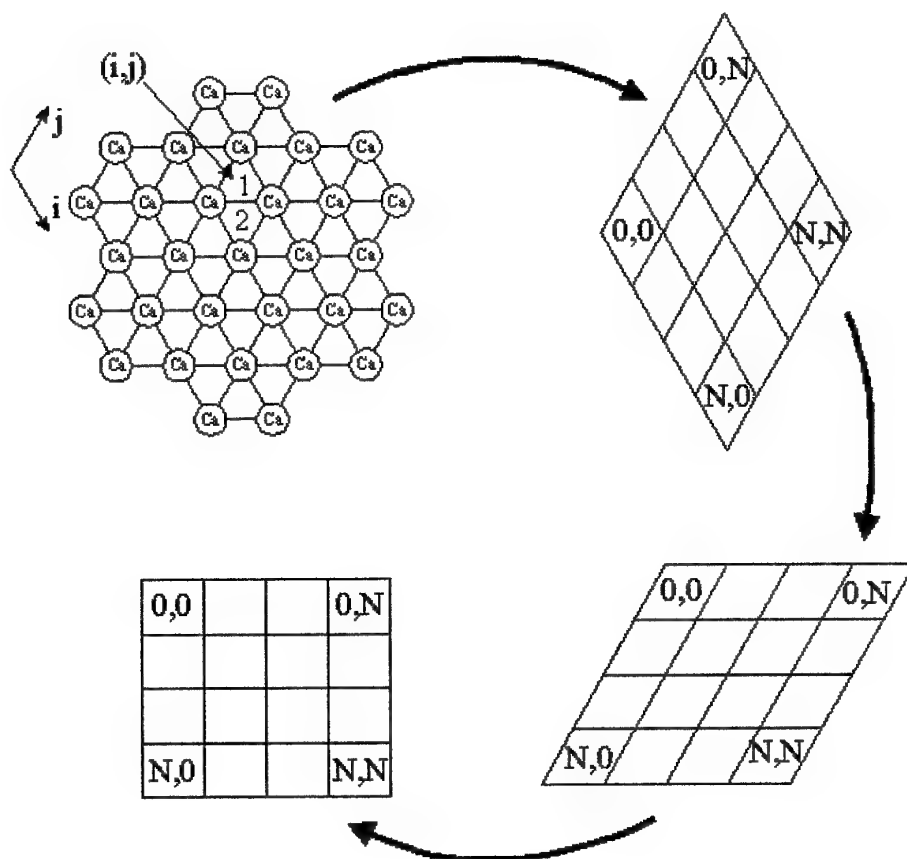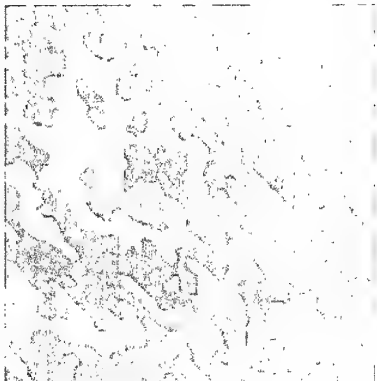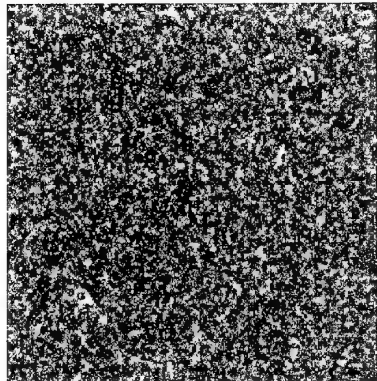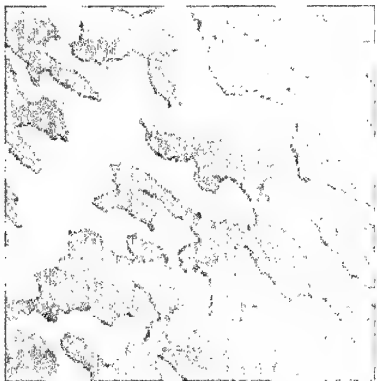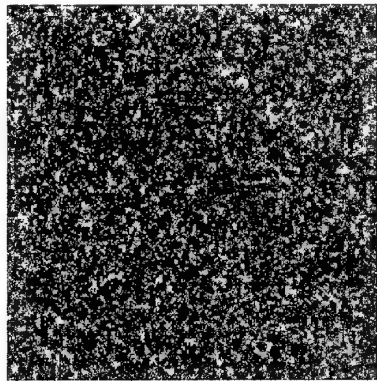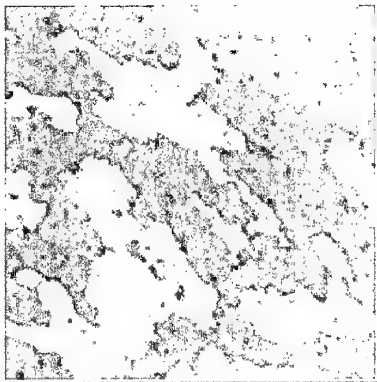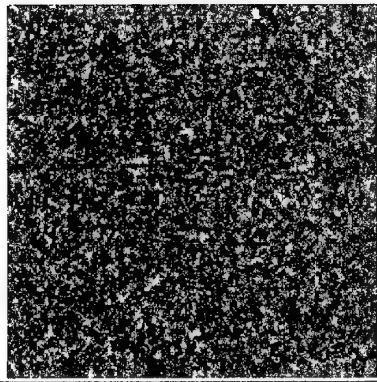
5 Results

The following are typical structures evolved for a series of temperatures and fluxes for both argon (left hand side) and neon (right hand side) on a calcium (111) surface. These results may be viewed as mpeg movies in the electronic version (http://abulafia.mt.ic.ac.uk/USAF/).

Ar on Ca, T= 3 K, 15% flux	Ne on Ca, T= 3 K, 15% flux
Ar on Ca, T= 23 K, 15% flux	Ne on Ca, T= 23 K, 15% flux
Ar on Ca, T= 33 K, 15% flux	Ne on Ca, T= 33 K, 15% flux

Ar on Ca, T= 43 K, 15% flux	Ne on Ca, T= 43 K, 15% flux
Ar on Ca, T= 53 K, 15% flux	Ne on Ca, T= 53 K, 15% flux
Ar on Ca, T= 63 K, 15% flux	Ne on Ca, T= 63 K, 15% flux

Ar on Ca, T= 93 K, 15% flux	Ne on Ca, T= 93 K, 15% flux
Ar on Ca, T= 123 K, 15% flux	Ne on Ca, T= 123 K, 15% flux
Ar on Ca, T= 143 K, 15% flux	Ne on Ca, T= 143 K, 15% flux

Ar on Ca, T= 170 K, 15% flux	Ne on Ca, T= 170 K, 15% flux
Ar on Ca, T= 273 K, 15% flux	Ne on Ca, T= 273 K, 15% flux
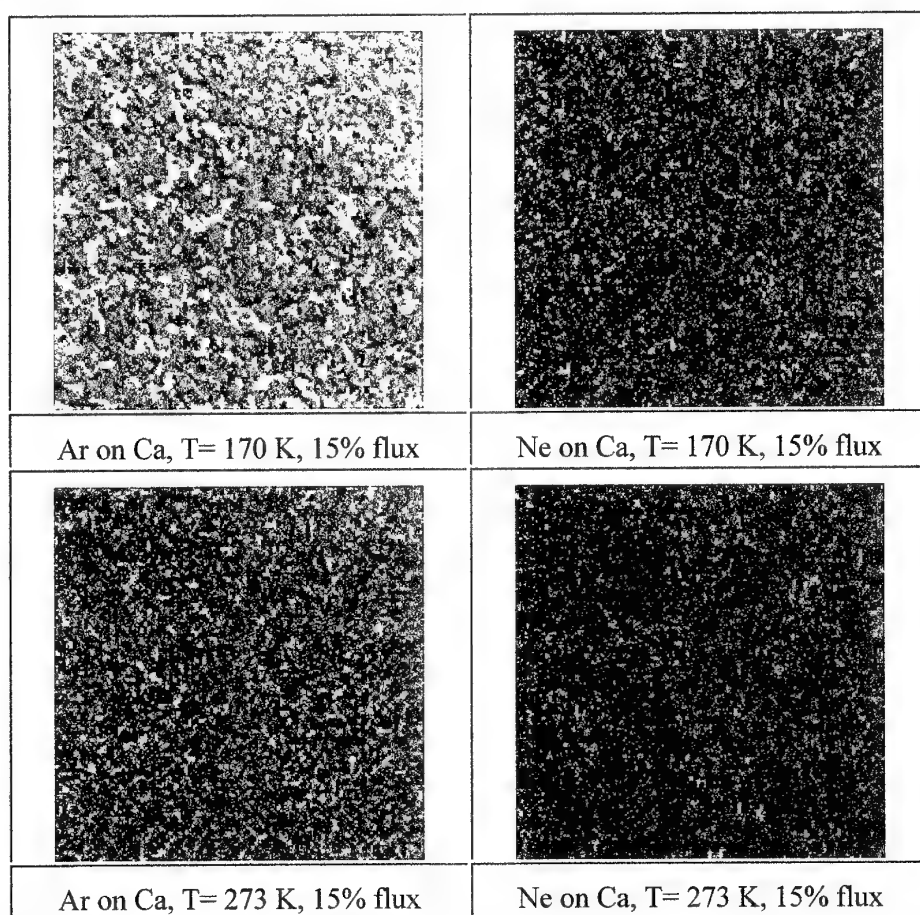
The first implication of these simulations is that for Ne and Ar, the rate of island growth is highly temperature dependent. Second, the temperature at which growth is a maximum is ~35K or Ne and ~130K for Ar. The increase in growth rate with temperature is clearly due to the increase in the kinetics. Presumably if the lower temperature simulations were implemented over more time steps, more pronounced island growth would eventually occur. However, at very low temperatures, this would take an inordinately long time. Finally, the limited island growth beyond the temperature of maximum growth rate is due to the instability of islands due to rapid evaporation.

In the next section we shall use these results to formulate an atomistic explanation for island growth. This is only possible because the CA rules are atomistically based. The potential importance of this work is now apparent. If we can understand how variations on the atomistic level modify the microstructure, we will be in a position to engineer microstructures by making modifications at the atomic level.

5.1 Interpretation

Consider the specific interface between two islands depicted below. Above each atom is its calculated attachment energy. It is clear that interface sites have lower attachment energies compared to sites which have a full complement of neighbours. This has two implications. First, interface atoms have a higher probability of evaporating. Second, atoms that are incident on a interface site are less likely to become attached. Consequently, the evolution of the atomic distribution is more active at interfaces.
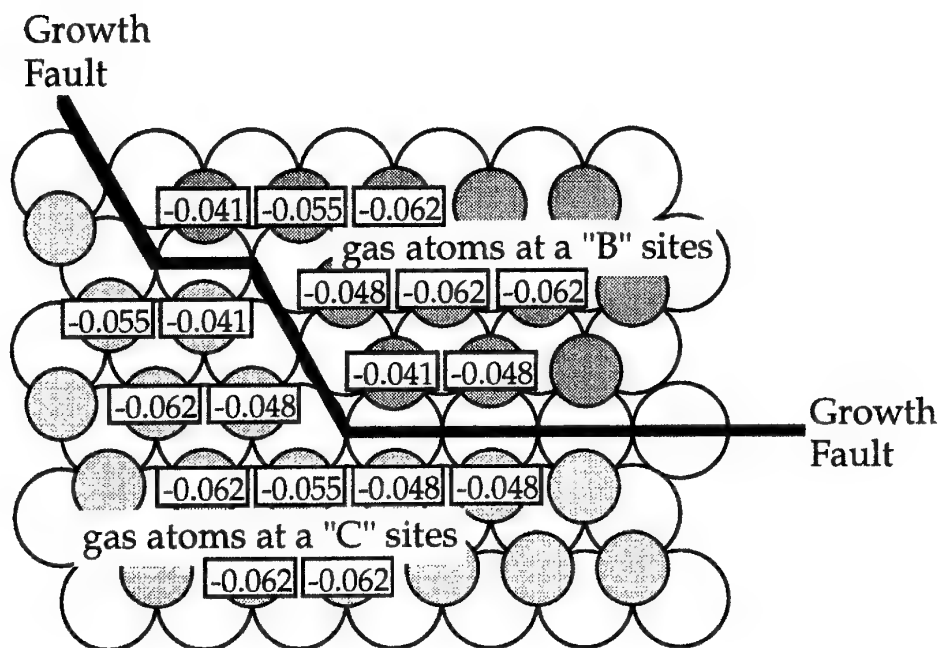
However, the situation is complicated by the fact that some interface sites have substantially lower attachment energies than others. Thus the more highly convoluted an interface, the more quickly it becomes modified through the evaporation attachment process. Furthermore, not only is there an energetic imperative for this to occur, there can also be a crystallographic hinderence effect. This can most easily be understood if we consider a straight (1,0,-1,0) interface.

Growth
Fault
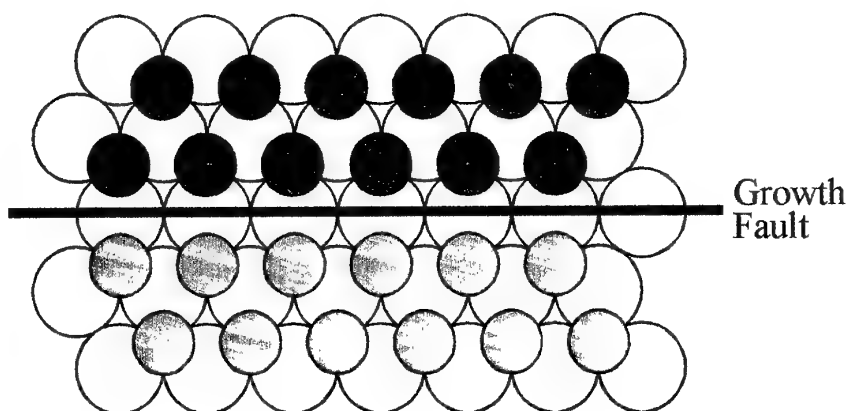
For the interface to progress upwards, expanding the "C" island, a "B" atom must be lost.
This is shown in the next figure.

Growth
Fault
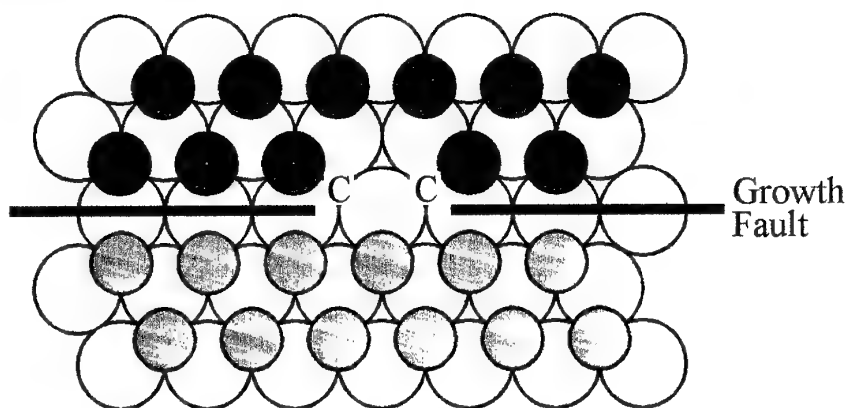
However, both of the potential "A" sites are hindered by "B" type atoms. Thus a second
"B" atom must evaporate, adjacent to the first site. This situation is shown in the next
figure.

Growth
Fault
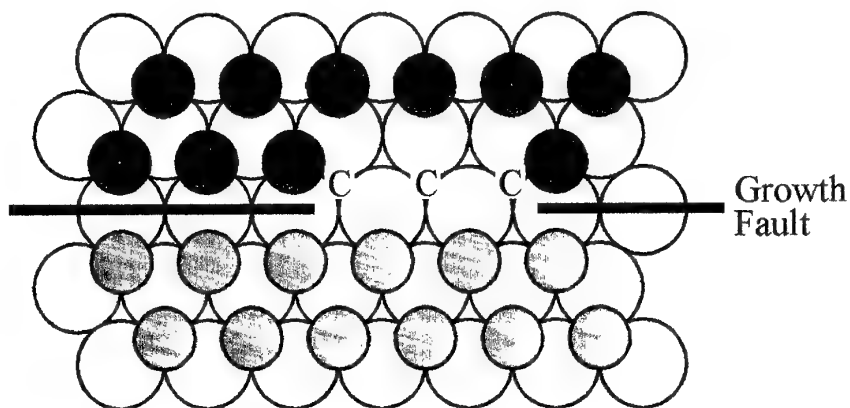
It is now possible for a single "C" type atom to attach itself to the surface, effectively
expanding the "C" island as shown. Of course, the probability that two atoms are lost
adjacent to each other is correspondingly small. Furthermore, this "C" type atom has only

two neighbouring "C" type atoms which means that its attachment energy is lower than if a "B" type atom were to reattach itself. Thus the expansion of a straight boundary is subject to energetic and probabalistic barriers.

Growth
Fault
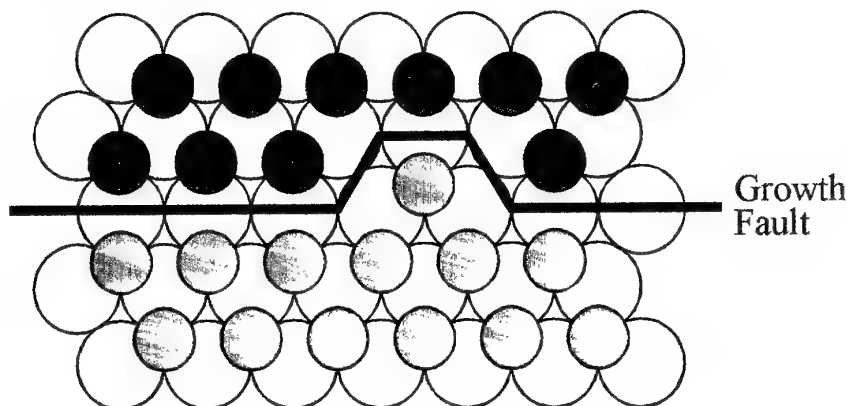
By running the argument the opposite way round it is possible to see that these type of convoluted structures will tend to be removed as the simulation progresses. Indeed, by applying this analysis to other situations, one can conclude that boundaries should straighten on an atomistic level. Of course, this is a well known experimental observation which is usually discussed in terms of surface tension.

At temperatures close to the maximum for island growth, the lower attachment energies of interface ions can have the effect of forming regions, adjacent to interfaces which are denuded of ions. These show up on the simulations as dark areas. However these are usually small and hard to see.

6   Possible limitations the CA model

One of the potential problems that has become apparent during the progress of this study concerns the reliability of predicted rates of island growth. Here we calculate an energetic advantage of atoms in the interior of islands over atoms at an interface region of between 10 - 50 %. The simulation is then run for 2,000 time steps which corresponds to approximately a microsecond. If the relative attachment energies were slightly different, the predicted temperatures at which the maximum in island growth occurs could be quite different. This is a general problem which should be given more attention. However, for many systems, experimental data may be available in which case, the energies could be learnt by running the simulation and matching this simple parameter.

In this model, each CA cell contains two sites of which only one may be occupied. This is fixed. Although we are able to simulate a greater number of atoms ($\sim 10^5$), over a far longer total time interval ($\sim 10^{-6}$ s) than any previous MD type simulation, for the modelling of a three dimensional atomic microstructure, we are still very limited. For example, a typical grain in a conventional microstructure would be at least ~ 0.1 micrometres across. This would encompass $\sim 5 \times 10^7$ atoms. Clearly we would wish to include more than one grain in any simulation! In addition, a typical heat treatment would last for at least 10^3 seconds. The approach to predicting real three dimensional

microstructural evolution will have to be fundamentally different. The most obvious modification would be to include multiple atomic sites in a single CA cell. Nevertheless, the properties of atoms in the CA cell could and probably would have to be learnt from a combination of smaller scale CA or even MD simulations. As such, we envisage a hierarchy of models which culminate in a full blown real scale simulation. In this regard, the scales of the present simulations are important.

7 Ideas for future work

7.1 Specific to the present code

In the short term, it would be very useful to run energy minimisation atomistic simulations of atoms in a variety of situations and formulate a more complete look-up table of attachment energies thereby formally completing the atomistic to CA loop.

Certainly a number of tools would be useful in providing analysis of the simulations. The first would be a way of reporting island size. This would allow us to quantify the extent of the grain growth over a given simulation time and grain growth rates as a function of temperature and pressure.

There are a number of additional topics which the present code should be used to address. The first is to introduce another atom type. A particularly interesting example would be xenon which due to its greater mass and higher polarizability would stick to the surface and attract neighbouring Ar or Ne atoms strongly. It is envisaged that xenon would then act as an island growth inhibitor, effectively pinning convoluted structures. Again this is not a technologically important example but it would expand our assessment of what this type of model can simulate successfully.

In these simulations, we start with an empty surface. As an alternative, we could begin with an idealised boundary and investigate how this evolves. For example, to what extent will a perfect straight (1,0,-1,0) boundary become convoluted over a period of time at a given temperature? Certainly it should, due to entropic effects, but to what extent is less clear.

It would also be possible to investigate the specific rate of shrinkage of a boundary as a function of island radius by initiating a simulation with a single circular island of specified radius.

7.2 Extensions to the present atomistic based code

It would be a simple matter to extend the present code to include diffusion since in this 2D context, this corresponds to activated hops into vacant sites. The activation energy can easily be calculated using energy minimisation atomistic simulation. Within islands, if migration is mediated by a single vacant site, this corresponds to "B" to "B" or "C" to "C" jumps. However, at a boundary between "B" and "C" islands, there is the possibility for "B" to "C" or "C" to "B" jumps which would have a lower activation energy. Interior "B"

to "C" to "B" double jumps are also possible if there are two adjacent vacant sites. It is important to bare in mind that diffusion effects have the potential to dominate the kinetics of island growth.

In the present code, the crystallographic orientations of surface islands are defined by the substrate coupled with the matched sizes of the Ne and Ar atoms. This gives rise to a very limited number of boundary orientations. In particular, it means that straight boundaries formed when islands of different orientation meet cannot be formed (i.e. boundaries that are not simple mirror images of each other). However, the manner in which such boundaries develop is of great potential importance, because matched sized systems are not the norm. One way forward in this regard is to use a coincidence lattice site theory approach where the boundary is composed of a periodically repeating set of local environment CA cells. Each CA cell would correspond to a set of atoms which would have evolution or migration properties which were predetermined using MD or quasiharmonic modelling techniques. For visualization, each CA cell would have as an attribute, a shape which was a function of the nearest neighbour relationships of the component atoms.

Another obvious limitation of the present code is that it can only simulate a 2D surface. However, it may not be too onerous a task to extend the code to 3D if the aim is to model a deposition process. The reason is that the principle factors in the kinetics of surface deposition, and hence thin layer morphologies are surface processes. Thus as a surface is covered with new material, on the time scale of surface deposition, atoms now beneath the surface may be regarded as inactive as far as the kinetics of the surface evolution is concerned. Of course, they will continue to influence the surface atoms through the attachment energy. The obvious way in which this could be achieved in terms of CA modelling is to assign each CA cell a height and a corresponding register of atoms. Thus as the simulation proceeds and the number of atoms in the system increases, the code does not become memory limited and remains efficient.

Finally, the code could be modified to model the deposition of molecular species. This would be particularly useful in modelling catalytic processes where molecules such as CO poison surfaces. The essential modification would be to associate each CA cell site with an orientation aspect. Also, each cell may have a number of sites each of which could potentially accommodate a molecule, or part of a molecule. In this way, a variety of molecular sizes could be attached in adjacent cells. This would have benefits for the modelling of deposition processes where atoms and molecules in the incident beam can interact with each other forming clusters in advance of deposition. Under such circumstances, momentum transfer effects may become important. Although this is an area in which there is little knowledge at present, it will be the focus of a forthcoming project which will employ MD techniques to study low energy atomic bombardment of ceramic surfaces (Grimes and Sickafus ICSTM from October 1997).

7.3   Beyond atomistic based code

One aspect of the overall debate that we have not been able to consider thoroughly enough is the extent to which the details of the local atomic structure influence the final

microstructure. Certainly we would expect the kinetics to be strongly controlled and hence the grain sizes but whether the type of microstructure (i.e. equiaxed , columnar etc.) is so critically affected is not so clear. Traditionally microstructural evolution models have been based on surface tension forces and diffusional mass transfer. Both of these could be translated into CA rule sets. For example, the local curvature of a boundary which crosses a CA cell is a parameter which would be effected by the curvature of adjacent cells and would control mass transport across the boundary within the cell. However, mass transport is highly anisotropic because of the details of the local crystal structure. Thus it is hard to envisage how neglecting the effects of crystallography can result in anything other than an empirically modified isotropic model.

Nevertheless, we cannot remain constrained to atomistic scale CA cells and expect to further improve computational efficiency to the extent necessary to undertake three dimensional microstructural modelling over long time scales. Thus it would seem inevitable that rather then associate specific crystallographic positions with a CA cell, it is more tractable to associate a crystallographic orientation and thereby introduce anisotropy into the rule set. Thus, the probability for mass transport, evaporation etc. would depend on boundary curvature and crystallographic orientation. Naturally this rule set would have to be compiled beforehand. Since experimental data will usually not be available, it will have to be derived using other modelling techniques. However, the reason for embarking on the present AR-CA study was partly because this type of data is computationally expensive to derive using MD or energy minimisation techniques. Thus the most likely solution would seem to be a hierarchy of methods starting with MD or energy minimisation, predicting rules for use in a AR-CA code which in turn provides the macroscopic rule set.

8   Concluding comments

The possibility of any favourable comparisons with microstructures in bulk solids would seem to be unlikely and of dubious validity at this stage. Nevertheless, the following figure is presented for the copper-phosphorus eutectic, an immiscible binary system.
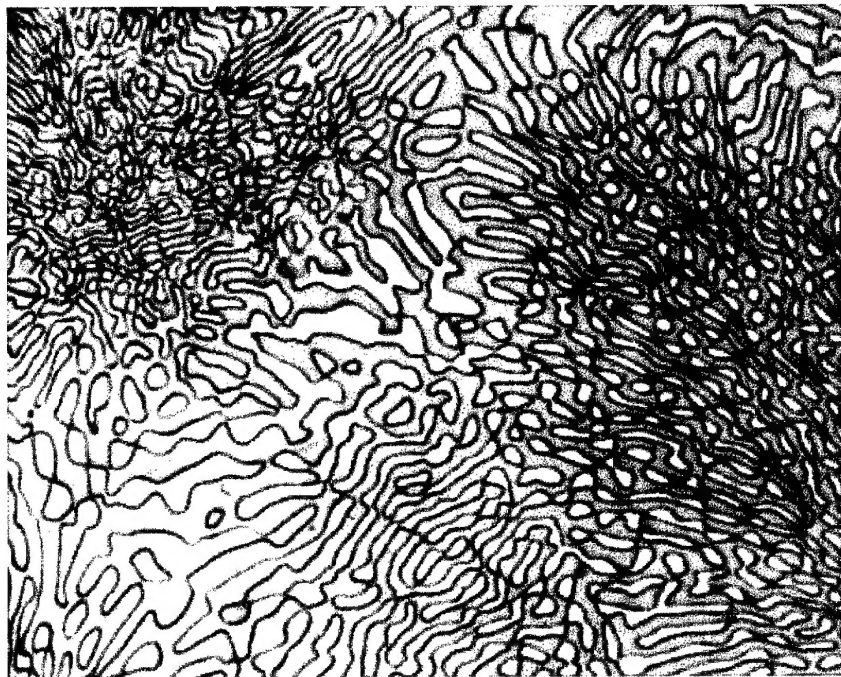
(Micrograph taken from "Materials Science" by Anderson, Leaver, Rawlings & Alexander)

Our present model assumes no attractive interaction between "B" type and "C" type islands but only a very short range repulsion. In this respect, the two types of gas atom islands are acting as if they were immiscible, although the immiscibility has a crystallographic rather than chemical origin. Furthermore, transport of atoms in this two dimensional system are via evaporation into the gas phase rather than by surface or solid state diffusion as might be expected in the three dimensional metallic system. Nevertheless, it may be that the basic model for a binary immiscibile system presented here is all that is necessary for this type of microstructure to be formed. The method of material transport may be largely responsible for the kinetics of growth rather than for the gross microstructural features. Therefore, although the authors wish to stress that considerably more work is necessary before firm conclusions can be drawn, (in particular diffusion rules must be introduced into the model) these results are certainly encouraging.